

**Table 1.7** Approximate Heating Value and Density of Some Representative Wastes

	Heating Value as Fired, Mj/kg	Density as Discarded kg/m <sup>3</sup>
Bitumen waste	38.5	892
Brown paper	16.7	80
Cardboard	15.8	107
Cork	26.4	190
Corrugated paper (loose)	16.4	59
Hardboard	19.0	535
Latex	23.3	713
Meat scraps	17.7	238
Nylon	31.7	119
Paraffin wax	43.3	832
Plastic-coated paper	17.1	80
Polyethylene film	46.0	12
Polypropylene	46.2	59
Polystyrene	41.1	104
Polyurethane foam	40.9	33
Resin-bonded fiberglass	45.4	589
Rubber	34.0	713
Shoe leather	16.8	321
Tar paper	26.7	268
Textile nonsynthetic waste	18.6	166
Textile synthetic waste	34.9	143
Vegetable food waste	20.9	178

SOURCE: *Chem. Eng.* 81 (18) 38 (1974)

## Biogas

Methane, produced by the decay of vegetable matter, was early identified as combustible "swamp gas." This highly desirable fuel was obtained by fermentation of sewage in Decatur, Ill. as early as 1934 and was used for heating and in internal combustion engines for pumping. Attention is currently focused on methane generation from large cattle feedlots<sup>19</sup> for distribution to towns; on smaller dairy farms it is being used on the farm itself. Several large demonstration plants are functioning well and many small units are in daily use. The total amount produced is small but of great significance locally.

## Solar Energy

There are two serious problems that restrict the use of solar energy. It is diffuse (averaging 1 kW/m<sup>2</sup>) and only intermittently available. There is much confusion regarding the meaning of the term "solar energy." Plants grow, winds blow, and waves are generated by the energy provided by the sun. Converters are needed to change the available solar energy into the forms usually needed by modern civilization—electricity and high-level heat.

<sup>19</sup>Anon., New Processes Harvest Farm Energy, *Chem. Week* 129 (15) 41 (1981)

Passive devices, such as south-facing windows, collect and effectively utilize solar heat. Active devices are being tried for concentrating solar energy to run boilers, which then produce power by conventional methods. The use of mirrors has enabled the great solar furnaces to attain very high temperatures. Photovoltaic cells convert solar energy into electricity directly. Water power and solar power are much alike in one respect: it is the large initial investment cost and the maintenance charges that offer the problem. The average roof receives more energy from the sun than the electrical energy which the house uses; the difficulty lies in the cost of capturing and converting it, storing it for use night and day throughout the year, and paying for and maintaining the expensive and complex devices. Solar cookers are quite practical in tropical countries but have never been acceptable to the cooks. Solar water heaters are quite popular on the oceanic islands, which are chronically short of fuel, and even enjoyed a brief (1936-1941) popularity in Florida,<sup>20</sup> but they proved uneconomical because of maintenance problems. Higher fuel costs have made solar hot water heaters again attractive, so a great many are currently being installed. It is probable that their better construction materials will make the solar heaters being installed today more attractive and competitive investments. A considerable number of new installations are taking place. For example, 8598 solar swimming pool heaters, 2910 domestic hot water heaters, 1787 space heaters, 234 space coolers, and 231 industrial processing units were installed in the United States in 1979.<sup>21</sup>

Photovoltaic devices are currently serving satisfactorily in watches and calculators, and as sources of electrical power for electronic devices in isolated areas.<sup>22</sup> The probability is quite small that solar energy will be a major source of power in this century. One major reason is that the large amount of material that must be assembled to take advantage of this diffuse source is greater than our industry could create if extensive use was made of solar power. Put another way, the amount of energy required to build the apparatus would not be recovered for many years.

### ***Ethanol from Biomass<sup>23</sup>***

Countries with favorable growing conditions for rapid production of biomass and with major oil shortages are experimenting with ethanol as an automotive fuel. U.S. attempts to use grain-derived alcohol as automotive fuel in the 1930s foundered on high cost, difficulty of maintaining alcohol-gas mixtures, and indifference. The same difficulties exist today. A bushel of grain produces at most 9.5 L of ethanol. Ordinary distillation produces only 95% ethanol, this will not mix with gasoline unless the last 5% of water is removed, and this requires an expensive additional process. Once mixed, alcohol-gasoline mixtures separate if any water enters the system, and this is almost impossible to prevent. None of these problems exist when pure

<sup>20</sup>Scott. What Became of Solar Water Heating? *CHEMTECH* 11 (6) 328 (1981).

<sup>21</sup>*Statistical Abstract of the United States*, 1980.

<sup>22</sup>Solar Cells Are Getting a Big Buildup, *Chem. Week* 127 (21) 46 (1980); Davison, Harris, and Martin, Storing Sunlight Underground. *CHEMTECH* 5 (12) 736 (1975); A Shakedown Shapes Up in Photovoltaics. *Chem. Week* 130 (5) 33 (1982).

<sup>23</sup>Fong, Jones, and Semrau, Costs of Producing Ethanol from Biomass. *Chem. Eng. Prog.* 79 (9) 39 (1980); Emert and Katzen, Gulf's Cellulose-to-Ethanol Process. *CHEMTECH* 10 (10) 610 (1980); Biomass to Ethanol without Fermentation. *Chem. Week* 125 (22) 38 (1979).

ethanol is used as fuel, except the cost. Cellulose hydrolysis to glucose followed by fermentation appears to be more promising as a source of fuel alcohol than other options currently considered. Because much forest land is not suitable for agriculture, the use of wood would not reduce the food supply. Attempts to require 10 percent of biomass-derived ethanol in domestic gasoline are politically acceptable to grain producers but economically impossible. Brazil is engaged in major production of motor fuel ethanol from sugar cane and appears to be doing quite well.<sup>24</sup>

## ***Vegetable Oils***

There is no doubt whatever that a wide variety of vegetable oils can be used, particularly as diesel fuels, with little or no additional processing. Prices are extremely high, however, and most such oils now produced are needed and are more valuable as food.

## ***Ocean Thermal***

A large potential for power production exists because of the difference in temperature between the ocean surface and its depths, particularly near the equator.

These differences can be used to drive machines which can produce electricity. A small land-based plant utilizing this principle has been built on the island of Nauru<sup>25</sup> by the Japanese, and the United States has two small units on Hawaii. Other countries (France, India, the Netherlands) are also engaged in research projects.

## ***Pipeline Hydrogen***

Hydrogen may become an important secondary energy form if problems of generating, storage, and transportation can be solved. Like electricity, hydrogen requires some other source of energy for its production. Once produced, however, hydrogen holds the promise of significant technical and economic advantages over its competition. For example, preliminary calculations show that pipelining hydrogen should be cheaper than transporting electricity by wire. Arguments, currently unresolved, surround costs and the possibility that cheaper methods of manufacture may be possible by unconventional means.

## ***Fusion***

Although there is much talk about it, there is as yet no process that produces fusion power and no assurance that there will ever be. Ultimately, the future of humankind as an energy-using creature may depend on the development of the fusion process. Enthusiasts predict that this method will be totally nonpolluting, be free of harmful by-products, and pose low risks. Some such ideas were advanced when nuclear energy first appeared. It was said that the cost

<sup>24</sup>Goodrich, Brazil's Alcohol Motor Fuel Problem. *Chem. Eng. Prog.* 78 (1) 29 (1982)

<sup>25</sup>Kohn et al., OTEC Gets Less Funding, but Stays Afloat. *Chem. Eng.* 89 (3) 43 (1982)

of energy would become so cheap that it would be given away. Disadvantages have a way of appearing after a new process becomes commercially operative.

A nuclear fusion reactor is a device in which controlled, self-sustaining nuclear fusion reactions may be carried out to produce useful power. Such a device does not now exist. Fusion is now carried out in extremely hot but tenuous fuel gas mixtures of hydrogen, helium, or lithium isotopes.

## AIR CONDITIONING

Control of temperature, humidity, and cleanliness of air is essential for human comfort in the hotter parts of the country and for the operation of many chemical processes. Artificial fiber production, certain pharmaceuticals, and photographic materials are particularly sensitive to ambient temperature. Efficient refrigeration processes combined with careful control of the humidity make the processes reasonably priced, but cooling still remains quite expensive. The design of air-conditioning units should usually be left to experts.

## REFRIGERATION

Removal of heat from a substance results in its cooling. The term refrigeration is usually applied to cooling below ambient temperature. Reactors frequently require use of refrigeration. The following processes could not proceed without refrigeration: manufacture of azo dyes, freezing out isomers from each other and/or impurities, food and beverage preservation, catalytic manufacture of ethyl chloride from ethylene and anhydrous hydrogen chloride at  $-5^{\circ}\text{C}$  under pressure, the production of "cold" rubber by polymerization at  $5^{\circ}\text{C}$  or lower, and the freezing of mercury at  $-73^{\circ}\text{C}$  into complex molds that are coated by repeated dipping into ceramic slurry followed by melting out of the mercury. Refrigeration operations involve a change in phase of a substance so that it will be capable of abstracting heat, such as the vaporization of ammonia or the melting of ice. Mechanical refrigeration can be divided into two general types: the *compression* system and the *absorption* system. Both systems

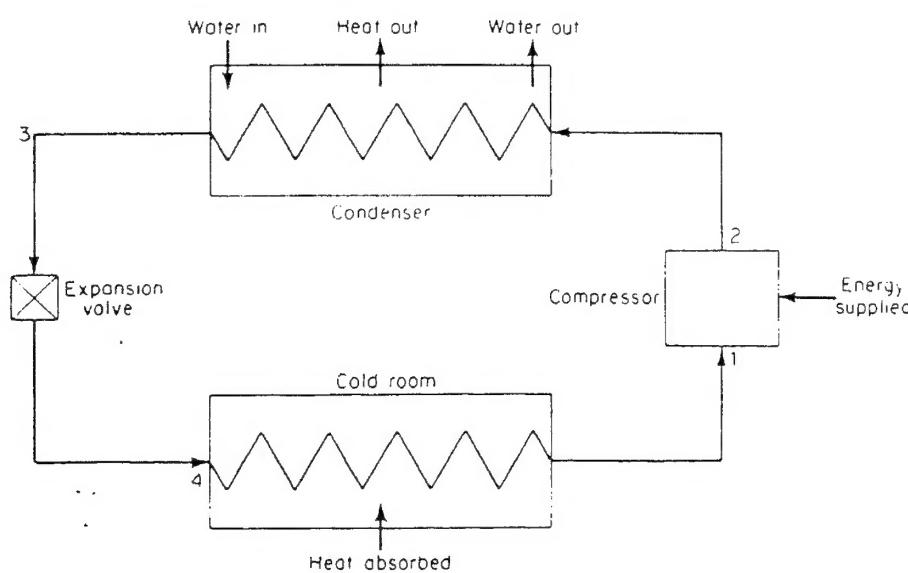


Fig. 1.7. Compression system for refrigeration

**Table 1.8** Properties of Refrigerating Agents

Refrigerant	Boiling Point at 101 kPa, °C	Critical Temperature, °C	Critical Pressure, MPa	Latent Heat at 101 kPa, kJ/kg
Ammonia (NH <sub>3</sub> )	-33	132	11.41	1370
Carbon dioxide (CO <sub>2</sub> )	-78°	31	7.47	293†
Sulfur dioxide (SO <sub>2</sub> )	-10	157	7.95	388
Methyl chloride (CH <sub>3</sub> Cl)	-24	143	6.73	428
Ethyl chloride (C <sub>2</sub> H <sub>5</sub> Cl)	+13	187	5.32	391
Freon-12 (CCl <sub>2</sub> F <sub>2</sub> )	-29	112	4.05	167
Propane (C <sub>3</sub> H <sub>8</sub> )	-43	97	4.29	370

\*Sublimes

†Latent heat at -29°C and 1521 kPa.

cause the refrigerant to absorb heat at low temperature by vaporization and to give up this heat elsewhere at higher temperature by condensation. The absorption system is used mainly in household units, but finds economical industrial application where cheap exhaust steam is available.

An ammonia refrigeration plant is a typical illustration of the vapor-compression system and is shown in Fig. 1.7. Table 1.8 gives properties of common refrigerating agents.

## SELECTED REFERENCES

Burke, B. L.: *Energy from the Wind—An Annotated Bibliography*, Colorado State Univ., Fort Collins, Colo., 1975.

Christian, S. D. and J. Zuckerman (eds.): *Energy and the Chemical Sciences*, Pergamon, Elmsford, N.Y., 1978.

DeRenzo, D.: *Energy from Bioconversion of Waste Materials*, Noyes, Park Ridge, N.J., 1977.

Dix, S. M.: *Energy: A Critical Decision for the U.S. Economy*, Energy Education Publ., Grand Rapids, Mich., 1977.

Doann, H. A.: *Alcohol Fuels: Policies, Production, and Potential*, Westview Press, Denver, 1982.

El Hinnawi, E. and A. K. Biswas (eds.): *Renewable Sources of Energy and the Environment*, Tycally, Intl. Publ., Dublin, 1981.

Grainger, I. and J. Gibson: *Coal Utilization Technology, Economics, and Policy*, Halsted, New York, 1981.

Greely, R. S., R. P. Ouellette, and P. N. Cheremisinoff: *Solar Heating and Cooling of Buildings*, Ann Arbor Sci. Publ., Ann Arbor, 1981.

Ion, D. C.: *Availability of World Energy Resources*, Graham and Trotman, London, 1975.

McMullan, J. T.: *Energy Sources and Supply*, Wiley, New York, 1976.

McRae, A., J. L. Dudas, and H. Rowland: *The Energy Source Book*, Aspen Systems Corp., 1977.

National Academy of Sciences: *Energy in Transition, 1985-2010*, San Francisco, 1979.

Oniciu, L.: *Fuel Cells*, Abacus Press, Tunbridge Wells, Great Britain, 1976.

Paul, J. K.: *Solar Heating and Cooling*, Noyes, Park Ridge, N.J., 1977.

Perelman, L. J., A. W. Giebelhaus, and M. D. Yokell (eds.): *Energy Transitions, Long Term Perspectives*, Westview Press, Boulder, Colo.

Ranney, M. W.: *Oil Shale and Tar Sands Technology*, Noyes, Park Ridge, N.J., 1981.

Rider, D. K.: *Energy: Hydrocarbon Fuels and Chemical Resources*, Wiley, New York, 1981.

Stamper, E. and R. L. Koral (eds.): *Handbook of Air Conditioning, Heating, and Ventilating*, 3d ed., Industrial Press, New York, 1979.

Stauffer, H. C. (ed.): *Oil Shale, Tar Sands, and Related Materials*, ACS, Columbus, Ohio, Houston, Tex., 1980.

*Two Energy Futures: A National Choice for the Eighties*, American Petroleum Institute, Houston, Tex., 1980.

Yen, T. F.: *Science and Technology of Oil Shale*, Ann Arbor Sci. Publ., Ann Arbor, 1976.

# Chapter 2

## Coal Chemicals

Most chemicals from coal were initially obtained by destructive distillation, furnishing chiefly aromatics. In recent years, a substantial production of aromatics, particularly benzene, toluene, xylene, naphthalene, and methylnaphthalenes, has been obtained by processing petrochemicals (Chap. 38). With the advancing application of chemical conversion of coal, many more chemicals can be made from coal whenever it is economical to do so. Coal chemicals, however, except for metallurgical coke, are now in a very competitive field. Table 2.1 summarizes chemicals produced from coal as presented in this chapter and elsewhere in this book (see also Fig. 2.1 for many coal chemicals). Coal is the country's fundamental fuel, but petrochemicals now furnish most of the basic raw materials for many essential industries from dyes, medicines, pesticides, and elastomers to modern plastics. Coal forms the world's largest reserve of concentrated raw material<sup>1</sup> from which chemicals can be extracted and produced, and it also is a cheap source of heat and power used for processing. Although production of gas and aromatics from coal has been curtailed by petrochemical and natural gas competition, much new research and development is being conducted by U.S. government agencies and by private industry. In Chap. 3, on fuel gases, reference is made to the intense efforts to manufacture a fuel gas of high heating value and to supply demands for such gas. These efforts must also supply a substitute for natural gas as its supply diminishes. Other research is directed to making new or old chemicals from coal, lignite, and shale through improved technology and to continuing investigations with the aim of eventually supplying motor fuels and other organic chemicals from coal<sup>2</sup> at competitive prices.

### THE DESTRUCTIVE DISTILLATION OF COAL<sup>3</sup>

When coal is thermally pyrolyzed or distilled by heating without contact with air, it is converted into a variety of solid, liquid, and gaseous products. The nature and amount of each

<sup>1</sup>OCR Calls for Petrochemicals from Coal, *Chem. Eng. News* 47 (1) 40 (1969).

<sup>2</sup>Process Utilizes Coal-derived Alkylphenols, *Chem. Eng. News* 59 (48) 32 (1981); Perry, Coal Conversion Technology, *Chem. Eng.* 81 (15) 88 (1974); Spitz, Petrochemicals from Coal, *CHEMTECH* 7 (5) 297 (1977); Harris et. al., Chemicals from Coal, *CHEMTECH* 11 (12) 764 (1981).

<sup>3</sup>Lowry, *Chemistry of Coal Utilization*, Supplementary Volume, Wiley, New York, 1963 (121 references); Elliott, *Chemistry of Coal Utilization*, Second Supplementary Volume, Wiley-Interscience, New York, 1981 (encyclopedic); Berkowitz, *An Introduction to Coal Technology*, Academic, New York, 1979.

**Table 2.1** Chemicals from Coal

Chemical Conversion Process	Products and Procedures (numbers refer to chapters)
a. Carbonization, pyrolysis of coal lignite, and carboniferous shales (destructive distillation)	Coal-tar aromatics, benzene and homologs, phenol and homologs naphthalene, anthracene phenanthrene, etc (5). High-temperature coke (5), low-temperature coke (5).
b. Reduction and refining of ores	Carbon for pigments (8), carbon for electrodes (5,8), structural material (8), activated carbon (8).
c. Gasification (cf. g and j) Blue and producer gas are very minor	Iron, ferro alloys, etc., aluminum (14), magnesium (14). Coal gas (6), blue water gas (6), producer gas (6), peak gas (6), synthesis gas (6), CO <sub>2</sub> liquid and dry ice (7).
d. Combustion for comfort heating and power generation	Electric power utilities (4), comfort heating, retail deliveries (4), fly ash (4), sintered ashes for filters and concrete (4).
e. Combustion for process heating	Heat for manufacture of lime (10), cement (10), ceramics (9), steel and rolling mills.
f. Reduction, chemical	Sodium sulfite (11,12), sodium sulfide (12), barium sulfide (20), phosphorus (16).
g. Hydrogenation and hydrogenolysis, catalytic	Carbide process for aromatics (5), hydrogenation of coal Bergius process (5), Fischer-Tropsch liquid fuels (5,6), catalytic methanation of synthesis and pyrolysis gases (5,6).
h. Demethylation	Benzene from toluene or xylene (37), naphthalene from methylnaphthalenes (37).
i. Hydrolysis, alkaline	Mixed aromatics (5).
j. Oxidation, partial (controlled) and complete	Synthesis gas (7) for NH <sub>3</sub> , CH <sub>3</sub> OH etc., hydrogen (7), coal acids (5), carbon monoxide (7).
k. Electrothermal	Graphite (8) and electrodes (8), abrasives silicon carbide (15), calcium carbide (15), cyanamide (18), carbon disulfide (15,38).
l. Sulfur recovery	H <sub>2</sub> S from gas (6,7).
m. Sulfonation	Pyrite from coal.
n. Solvent extraction of coal	Ion exchange, water softeners (3). Ashless coal, montan wax (28), humic acids, coumarone resins (34).

SOURCES: Lowry, *Chemistry of Coal Utilization*, vols 1 and 2, Wiley, New York, 1945, suppl. vol., 1963; Future for Fossils, *Chem. Week* 115 (15) 46 (1974). Perry, op cit (several flowcharts); Iammartino, *Chem. Eng.* 81 (21) 68 (1974). McMath et al, *Coal Processing; A Pyrolysis Reaction for Coal Gasification*, *Chem. Eng. Prog.* 70 6-72 (1974); *Chemical Communication Shows Promise for Coal*, *Chem. Eng. News* 52 35-16 (1974); UOP Set to Scale Up Oil-from-Coal Process, *Chem. Eng. News* 52 38-7 (1974).

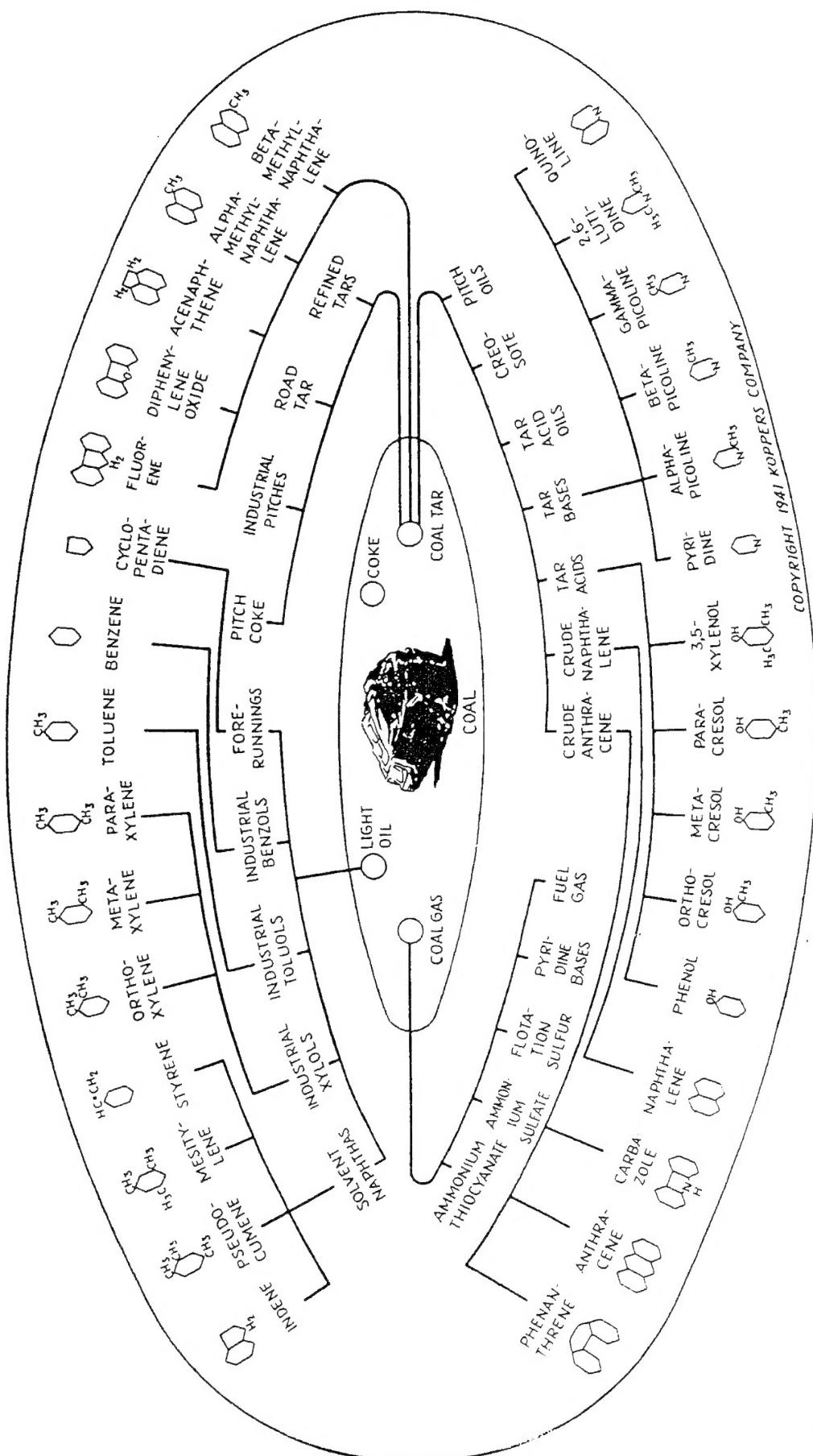


Fig. 2.1. How many grandchildren has a lump of coal? (Koppers Co., Inc.)

product depends upon the temperature used in the pyrolysis and the variety of the coal used. In ordinary practice, coke-oven temperatures are maintained above 900°C but may range anywhere from 500 to 1000°C. The principal product by weight is coke. If a plant uses temperatures from 450 to 700°C, the process is termed *low-temperature carbonization*; with temperatures above 900°C it is designated *high-temperature carbonization*. In low-temperature carbonization the quantity of gaseous products is small and that of the liquid products is relatively large, whereas in high-temperature carbonization the yield of gaseous products is larger than the yield of liquid products, the production of tar being relatively low.

Low-temperature carbonization produces liquids strikingly different from those produced by high-temperature carbonization, even when using the same coal. Low-temperature liquids contain more tar-acids and tar-bases than high-temperature liquids. The market for low-temperature liquids is not yet well-established. With high-temperature carbonization, the liquid products are water, tar, and crude light oil. The gaseous products are hydrogen, methane, ethylene, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, and nitrogen. The products other than coke are collectively known as coal chemicals, or *by-products*.

The destructive distillation of coal, or its carbonization, is really a striking example of chemical conversion, or the process of pyrolysis. This chapter outlines the equipment needed to carry out, on a commercial scale, the basic chemical changes that take place. The chemical theory of the pyrolysis of coal<sup>4</sup> indicates the following step-by-step decomposition.

1. As the temperature is raised, the aliphatic carbon-carbon bonds break first. Reaction begins below 200°C.

2. Carbon-hydrogen linkages break next at or near 600°C

3. The elimination of heterocycle complexes and progressive aromatization are the essential reactions taking place during the decomposition as the carbonization proceeds.

4. The molecular weights of the intermediate products regularly decrease as the temperature rises. Water, carbon monoxide, hydrogen, methane, and other hydrocarbons are evolved.

5. Decomposition is at a maximum between 600 and 800°C. All the above reactions vary markedly in their extent depending on the rate of heating as well as the temperature attained.

Hill and Lyon<sup>5</sup> suggest that "coal consists of large heterocyclic nuclei-monomers, with alkyl side chains held together by three-dimensional C—C groups, and includes functional oxygen groups." (See Fig. 5.2.)

**HISTORICAL.** It is known that coke was an article of commerce among the Chinese over 2000 years ago, and in the Middle Ages it was used in the arts for domestic purposes. Nevertheless, it was not until 1620 that the production of coke in an oven was first recorded. Up until the middle of the nineteenth century, coal tar and coal-tar products were regarded as waste. Synthesis of the first coal-tar color, by Sir William Perkin in 1856, caused a great demand for coal tar, and it became a commercial product of increasing value. Perkin, with his discovery of the brilliant violet dye, mauve (Chap. 39), while attempting the synthesis of quinine through the oxidation of crude aniline in England, laid the foundation of the world's coal-tar-dye industry. In 1792, the first successful experiment involving the production of gas

<sup>4</sup>Fuchs and Sandhoff, Theory of Coal Pyrolysis, *Ind. Eng. Chem.* 34 (5) 567 (1942). Lowry, op. cit., p. 379.

<sup>5</sup>Hill and Lyon, A New Chemical Structure for Coal, *Ind. Eng. Chem.* 54 (6) 37 (1962). Elliott, op. cit.

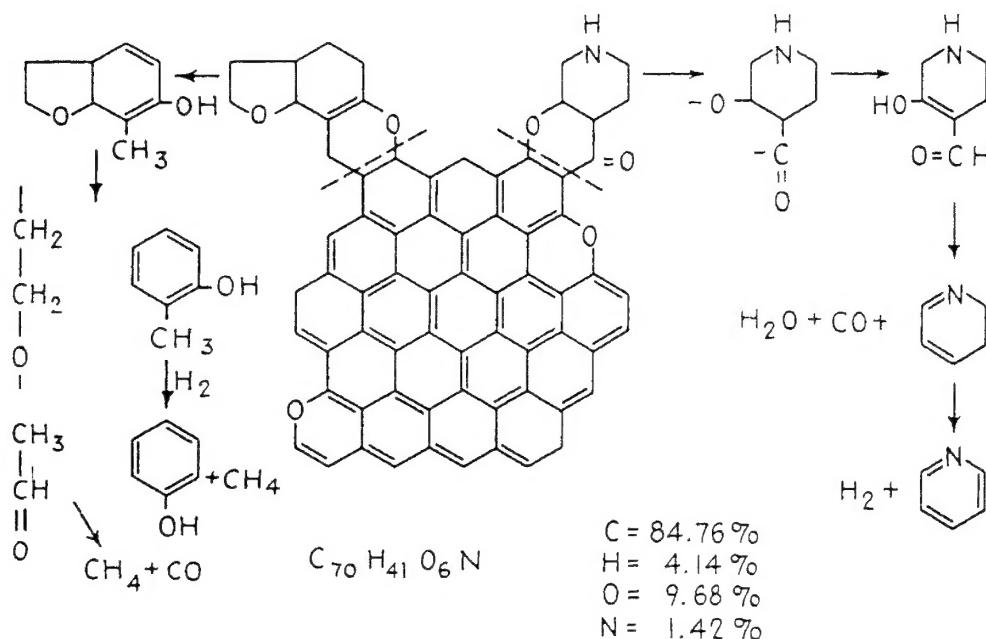


Fig. 2.2. Example of coal pyrolysis. (After Fuchs and Sandhoff)

from coal was carried out by William Murdoch, who made it possible to light the streets of London with gas in 1812. The first battery of Semet-Solvay ovens was erected in Syracuse, N.Y. in 1893.

**USES AND ECONOMICS.** Coke is the product of largest tonnage from the distillation of coal. The demand for coke depends on the demand for steel. About 98 percent of coal-tar production is from by-product ovens.<sup>6</sup> See Table 2.2 for data on crude aromatics from coal and petroleum. Until recent years aromatic crudes and the pure compounds derived therefrom were based exclusively on coal tar. Now that the petroleum industry supplies so many aromatics, the chief incentive in distilling coal is to supply coke for steel. The liquid products, comprising coal-tar and ammonia liquor, are not so large in volume as the solid products of coal distillation, but they are of importance to chemical-recovery ovens. A considerable volume of coal tar is still used as fuel, and for roofing and roads. Aromatics from petroleum and coal tar are made into dyes, intermediates, medicinals, flavors, perfumes, resins, rubber chemicals, and thousands of other useful products that are almost indispensable to our present civilization.

## COKING OF COAL

Although coke can also be made from petroleum (see Heavy Distillates, Chap. 37), the two main types of coking procedures for coal were the beehive and the by-product. Beehive coking is the obsolete, primitive method. In by-product ovens the carefully blended coal charge is heated on both sides so that heat travels toward the center and thus produces shorter and more solid pieces of coke than are made in the beehive oven. Air is excluded so that no burning takes place within the oven, the heat being supplied completely from the flues on

**Table 2.2** U.S. Production of Tar and Tar Crudes (in millions of liters except where noted otherwise)

Product	Production				
	1953	1964	1972	1979	1980
Crude light oil	1151	941	811	398	602
Intermediate light oil	4.0	20.4	14.0	n.a. <sup>6</sup>	n.a.
Light oil distillates					
Benzene, specification and industrial grades, total	919	2764	4741	6332	7585
Tar distillers	122	—	—	—	—
Coke-oven operators	672	450	302	231	192
Petroleum operators	239	2314	4439	6101	7396
Toluene, all grades, total	591	1874	3467	3823	3845
Tar distillers	17.7	—	—	—	—
Coke-oven operators	136	96.2	55.2	35.0	29.5
Petroleum operators	437	1777	3412	3788	3816
Xylene, total	430	1299	2798	3680	3434
Coke-oven operators	37.6	26.9	12.7	5.2	5.1
Petroleum operators	389	1272	2786	3675	3429
Solvent naphtha, total	59.3	—	—	—	—
Tar distillers	35.5	—	—	—	—
Coke-oven operators	23.0	17.0	10.7	5.1	—
Other light oil distillates, total	55.5	—	—	—	—
Tar distillers	32.4	—	—	—	—
Coke-oven operators	23.1	34.5	26.1	—	—
Pyridine crude bases, dry basis	2.09	1.76	—	—	—
Naphthalene, crude	125	193	186	—	—
Crude tar-acid oils	—	105	36.8	72.0	51.6
Creosote oil, dead oil	550	429	527	408	229
All other distillate products	70	—	—	—	—
Tar, road	416	211	113	—	—
Tar, miscellaneous uses, t	138	75.6	54.5	51.6	45.3
Pitch tar, t	1712	1706	1244	n.a.	1053
Hard tar, t	645	901	715	—	—

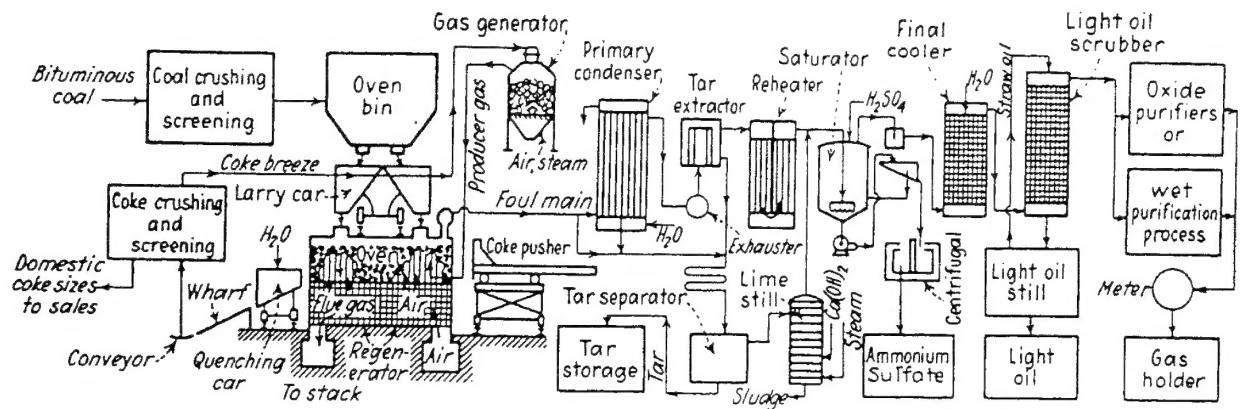
<sup>6</sup>n.a., not applicable<sup>7</sup>Where dashes occur, data are not available, usually because publication would disclose individual production figures. This is prohibited by law.SOURCE: *Synthetic Organic Chemicals* (International Tariff Commission), p. 108.

the sides. About 40 percent of the oven gas, after being stripped of its by-products, is returned and burned for the underfiring of the battery of ovens, and some is used for fuel gas locally.

Beehive coking disappeared from the United States because it was a small batch process and produced a very large amount of pollution. It continues to be used in many places abroad.

**BY-PRODUCT COKING.** The by-product coke oven is a narrow chamber, usually about 1.1 to 1.2 m long, 4 in high, and tapering in width from 0.4 to 0.6 m at one end to 0.35 to 0.4 m at the other. The ovens hold from 15 to 25 t of coal.<sup>6a</sup> These ovens are used for carbonizing coal only in large amounts and are built in batteries of 10 to 100 ovens. The general arrangement for the operation of a by-product coke oven with its various accessories, followed by the initial treatment of its by-products, is depicted<sup>7</sup> in Fig. 5.3.

<sup>6a</sup> t = 1000 kg<sup>7</sup>Lowry, op. cit., chap. 11, p. 461 (121 references) and Elliott, op. cit.



In order to produce: 0.28–0.35 Mm<sup>3</sup> of 20.5 MJ/m<sup>3</sup> gas; 700 kg coke; 38 L tar; 11.4 kg ammonium sulfate; 7.6–15.2 L light oil, the following materials are required.

Bituminous coal	1 t	Steam	200–600 kg
Sulfuric acid (60°Bé)	12.5 kg	Electricity	25 MJ
Lime	0.75–1 kg	Direct labor	0.8–1.3 work-h
Water	4150–8000 L		

Fig. 2.3. By-product coke-oven procedures.

The by-product coke oven is one of the most elaborate and costly of masonry structures and is erected with the closest attention to engineering details, so that it can withstand the severe strains incurred in its use and remain gastight even after the great expansion caused by the heating up. The oven block is built of refractory brick, with heating flues between the coking ovens, as shown in Fig. 2.4.

The individual by-product coke oven operates intermittently, but each oven is started and stopped at different times, so that the operation of the entire block continually produces gas of good average composition. A charge of finely crushed coal is dropped from a larry car through charging holes (usually four, though the generalized flowchart of Fig. 5.3 shows only two) in the top and into the oven, where the walls are at approximately 1100°C. The surface of the coal in the oven is leveled and the charging holes are then covered. Heating is carried out and the charge left in the oven until it is completely coked and the evolution of volatile matter has ceased. The average temperature at the center of the charge at the end of the heating period is usually about 980°C, and the average flue temperature is about 1290°C. Temperatures vary with the conditions of operation, the coking time, the width of the oven, and the type of coal, its moisture content, and its fineness of division. By-product ovens are no longer operated to make a large volume of high-grade coal tar or gas but to make the best quality furnace coke for steel mills. At the end of the coking time (approximately 17 h) the doors at the end of the oven are opened and the entire red-hot mass is pushed out through the oven from end to end in less than a minute by an electrically driven ram. The coke falls into a quenching car, which holds the charge from one oven. The coke is quenched with water, thus cooling it and preventing it from catching on fire. In the U.S.S.R. and Japan some plants use a "dry quenching" system, which recovers some of the sensible heat.

The gas from the destructive distillation of the coal, together with entrained liquid particles, passes upward through a cast-iron gooseneck into a horizontal steel pipe, which is connected to all the ovens in a series. This pipe is known as the collecting main and is sometimes called a hydraulic main. As the gas leaves the ovens, it is sprayed with weak ammonia water. This condenses some of the tar and ammonia from the gas into liquid. The liquids move

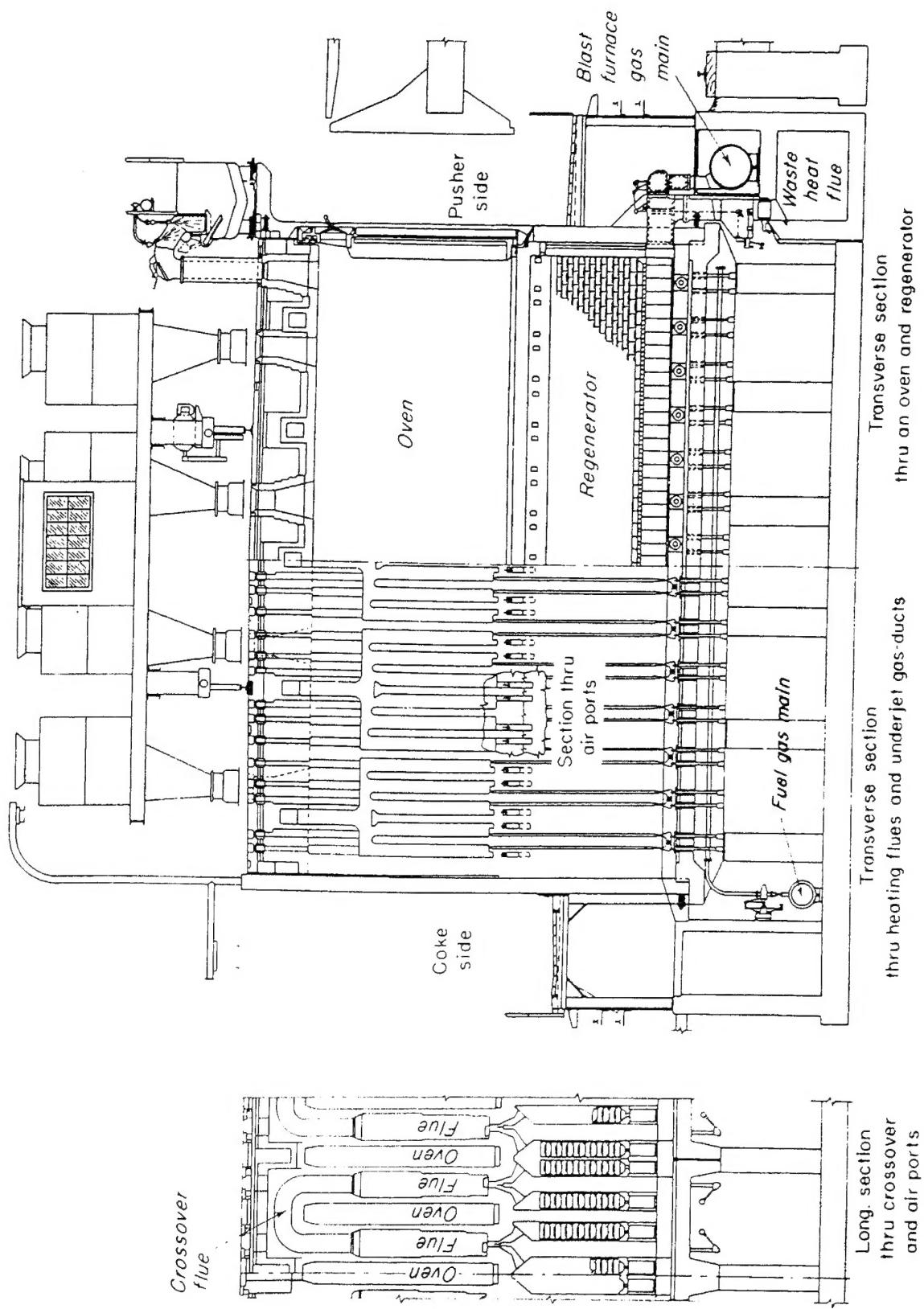


Fig. 24. Koppers Becker underjet low-differential combination coke oven with waste-gas recirculation. (Koppers Co., Inc.)

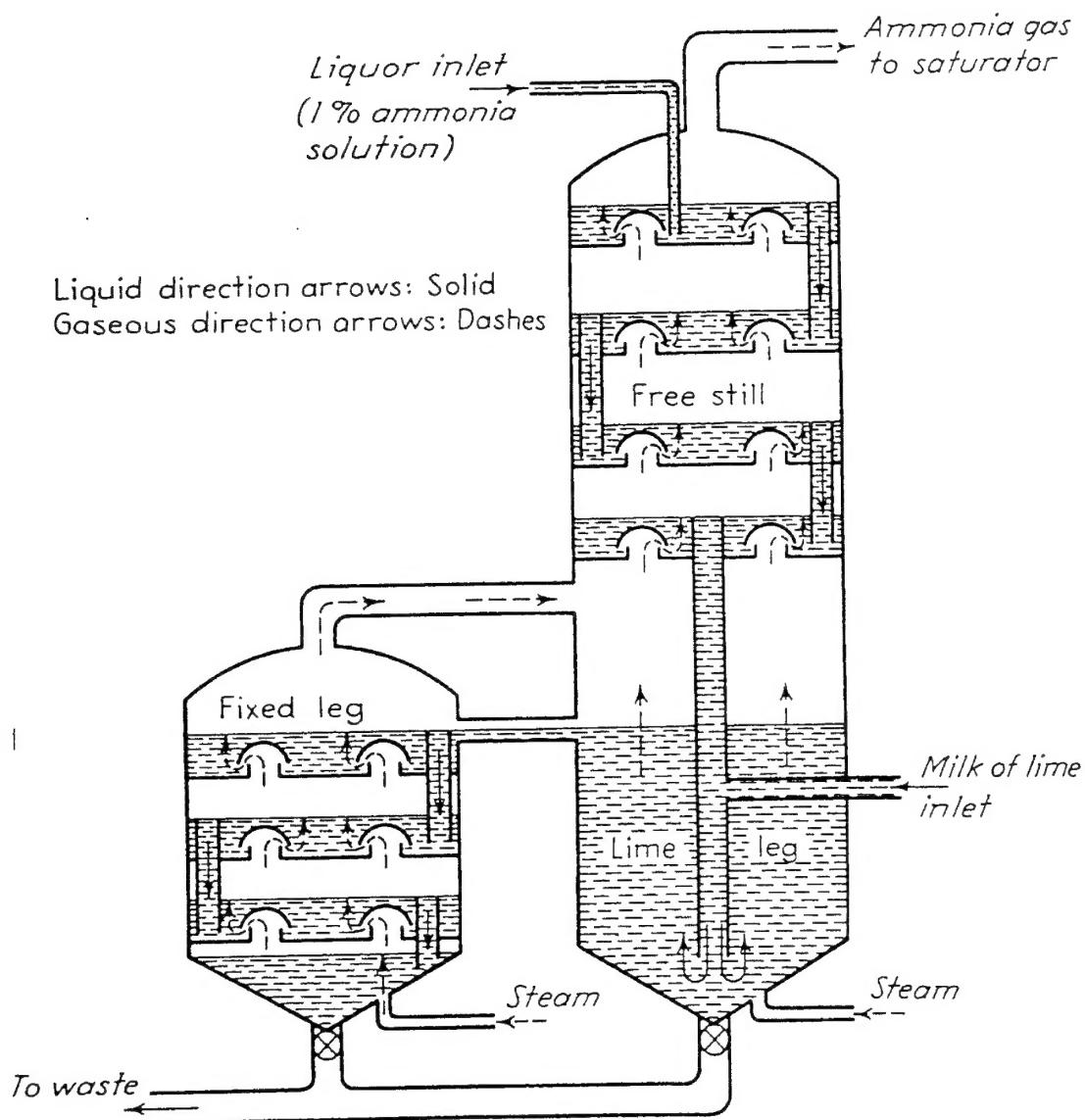


Fig. 2.5. Diagram of an ammonia still. It operates with a drain from the fixed leg opened sufficiently to prevent accumulation of liquor in this section. The drain from the lime leg is closed except for cleaning.

through the main along with the gases until a settling tank is reached, where separation is effected according to density. Some of the ammonia liquor is pumped back into the pipes to help condensation; the rest goes to the ammonia still (Fig. 2.5), which releases the ammonia for subsequent chemical combination in the saturator. All the tar flows to storage tanks for tar distillers or for fuel.<sup>8</sup>

Figure 2.3 can be divided into different steps, representing the flow of material through the various pieces of equipment, wherein the proper physical operation or chemical conversion takes place. Figure 2.3 may be thus broken down into the following sequences:

Coal is transferred, crushed, and screened.

Coal is charged to a hot, empty oven.

Coal is chemically transformed to coke and volatiles by pyrolysis.

Hot coke is pushed out of the oven, quenched, and transported.

<sup>8</sup>Lowry, op. cit., p. 462, for other types of ovens.

Condensable products of distillation are liquefied and collected in the hydraulic main. Foul gas is cooled, and tar extracted.

Ammonia is removed from gas as ammonium sulfate.

Gas is cooled and subjected to benzene and toluene removal by absorption in straw oil.

Hydrogen sulfide is removed.

Purified gas is metered and transferred to consumers.

The tar separated from the collecting main and the tar extractors or electrostatic precipitators is settled from ammonia liquor and, together with light oil, subjected to the sequences represented by the flowchart (Fig. 2.6). The pipe still is of the radiant-heated type. The crude tar feed inlet can be seen at the lower right. The tar is filtered and pumped through the reflux vapor-tar heat exchanger, economizer, pitch-tar heat exchanger into the top of the lower third of the distillation column and out at the bottom, to the circulating pumps and into the pipe still (where the crude tar joins 4 to 5 volumes of the circulating pitch and on finally to near the top of the distillation column). The vapors, steam distilled and superheated, pass overhead from the top of the tray-type distillation column, enter the bottom of the bubble-cap fractionating column, and are separated into four fractions 1, 2, 3, 4, with a residue 5, leaving at the bottom of this fractionating column. The product pitch, 6, cascades from the top of the distillation column down through the superheated steaming section to establish the desired pitch hardness and to strip this pitch of the higher-boiling volatile oils. It is then withdrawn from above the middle of the distillation column and conducted through the pitch-tar heat exchanger to storage. The products are:

	Product	Boiling Point, °C
Side stream 1	Light oil	to 170
Side stream 2	Carbolic oil	170-205
Side stream 3	Naphthalene oil	205-240
Side stream 4	Creosote or wash oil	240-280
Residue 5	The residue or anthracene	270-340
Pitch 6	Residuum or pitch	325-400

There are standby steam pumps in the event of failure of the motor-driven pumps. The Wilton principle of recirculation of hot pitch at 350°C, mixed with the crude tar at 120°C, raises the temperature of the pitch-tar leaving the pipe still to only 350°C and avoids thermal cracking and vaporization in the pipe still.

Koppers-Becker ovens are the most widely used vertical-flue ovens in the United States. The elevation is shown in Fig. 2.4. These ovens are all of the regenerative type and have individual heat regenerators, generally from side to side, underneath the oven. The gas burns upward, crosses over the top of the oven, comes downward on the other side, and exits through the regenerator oven underneath. The reversal of the air and waste gas flow is made from side to side every half hour.

Coke and char can be made by continuous processes, but the liquid products and the coke formed vary greatly from the products obtained from a by-product oven.

Low-temperature carbonization once looked promising as a method of producing fuel gas and reactive char, which is useful as a smokeless fuel for domestic heating. Several continuous processes, for example, the Lurgi-Spulgas retort, have had some success in Europe. In the